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**The Relation of the Surface Properties of the Teflons to  
Frictional Electrification by Polystyrene**

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  The friction and frictional electrification properties of Teflon TFE (polytetrafluoroethylene), Teflon PFA [tetrafluoroethylene-perfluoro-(alkyl vinyl ether) copolymer] and Teflon FEP (tetrafluoroethylene-hexafluoropropylene copolymer) have been studied by rubbing them against polystyrene. Potentials generated on the fluorocarbon polymers were measured by the classical Faraday ice-pail method. The relationship of surface energy and chemical constitution of the fluorocarbon surfaces to kinetic coefficient of friction $\mu_k$ and frictional electrification properties was investigated by using the		

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## 20. Abstract (Continued)

contact-angle technique. The lower surface energies, higher  $\mu_k$ , and higher potentials generated on the copolymers, compared with the behavior of TFE, has been explained as the effect of perfluoromethyl ( $\text{CF}_3$ ) groups and perfluorinated alkane side chains present in the surfaces of these materials. Annealing TFE lowers the surface energy and  $\mu_k$  slightly and reduces the potential generated to  $\frac{1}{4}$  the preannealed level. Annealing the copolymers causes a substantial reduction in surface energy and an increase in  $\mu_k$  but has varied effects on frictional electrification properties. Removal of the outermost layers by abrading the annealed polymers restores the surface energy to preannealed levels but has a varied effect on friction and frictional electrification properties. Some of the surface-energy change upon heating FEP may be related to changes in crystallinity, but most of it appears to arise from an increase in  $-\text{CF}_3$  groups in the surface. One of the most likely mechanisms involved in the frictional electrification of the fluorocarbon polymers appears to arise from the straining and rupturing of chemical bonds with the result that easily displaced electrons become vulnerable to trapping by the strongly electronegative fluorine atoms. The reason quantitatively reproducible frictional electrification measurements with solids are difficult to obtain is believed to be that the process of rubbing alters the nature of the contacting surfaces in a poorly reproducible manner.

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## THE RELATION OF THE SURFACE PROPERTIES OF THE TEFLONS TO FRICTIONAL ELECTRIFICATION BY POLYSTYRENE

### INTRODUCTION

The accumulation of electrical charges on solids rubbed together has been studied by a number of investigators over many years. It was customary to arrange the solids into *triboelectric* series somewhat analogous to the electrochemical potential series. The arrangement was such that any member of the series acquired a positive charge when rubbed against a member below it and a negative charge when rubbed by a member above it. Shaw [1] in reporting his own rather extensive triboelectric series in 1918 indicated that Wilcke had established a triboelectric series as early as 1759. Most of the materials studied by the early investigators were naturally occurring and included both inorganic and organic substances. However the assigned positions for some of the materials listed in the several proposed triboelectric series did not agree. Shaw [1] reported that heating glass caused a temporary reversal of charge sign when it was rubbed with silk. He concluded that most solids will alter their position in the triboelectric series if heated above a certain temperature, specific for each material. He also concluded that triboelectricity afforded a means of discriminating between materials which were otherwise apparently alike.

In 1927 Shaw [2] had reached the point in his research on triboelectricity where he concluded that it was impossible to devise a simple triboelectric series of one column to accommodate all solids. He cited several factors which altered the position of solids in the triboelectric series. Thirty years later Montgomery [3] stated that great variability still existed in the reproducibility of observations in static electrification. Interest in triboelectric series of solid materials declined until relatively recently, when widespread use of synthetic polymers, with their tendency to accumulate undesirable electrical charges, contributed to a renewed interest in the static electrification of solids [3]. Triboelectric series which include several synthetic polymers have been reported [4-6]. However, as Morris [7] pointed out, some agreement exists among the more recently proposed triboelectric series involving synthetic polymers, but there is little correlation when quantitative measurements are made. Harper [8a] and Montgomery [3] have indicated that static or frictional electrification of solids is not well understood and that several mechanisms may be involved. Both have pointed out relevant variables which influence the accuracy and reproducibility of data in the literature. Factors which may be responsible for some of the discrepancies noted include differences in the experimental methods employed, environmental conditions, variations in the chemical composition and homogeneity of the specimens, surface contaminants, and differences in methods of cleaning or preparing the specimens.

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Note: Manuscript submitted April 8, 1975.

One objective of this investigation has been to seek an improvement in the reproducibility of frictional electrification measurements by rubbing relatively well defined, chemically related solids against polystyrene. The simple, but fundamental, Faraday ice-pail method was used to measure the electrostatic charges. Three fluorocarbon polymers were chosen for study: Teflon TFE (polytetrafluoroethylene) and two copolymers. They were selected because of their chemical inertness, relative freedom from impurities, and insignificant water absorptivity and because their chemical relationship simplified molecular interpretation of their frictional electrification properties. Interpreting the effect of surface structure or constitution on electrification by friction is difficult because the very act of rubbing one solid against another may change the nature of the surfaces significantly. This is likely a major factor in the poor reproducibility of frictional electrification measurements. The contact angle (Fig. 1) of a sessile drop resting on a solid has long been used to measure the wettability of solids by liquids [9] and to determine the constitution of solid surfaces by Zisman [9a], Adams [9b], and others.

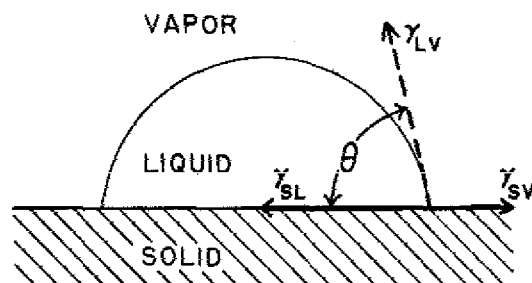


Fig. 1 — Schematic diagram of the contact angle ( $\theta$ ) formed by a sessile drop resting on a solid surface

That the contact-angle technique can be used to study the nature of surfaces without altering them structurally makes the application of this method attractive. In the present investigation the frictional electrification characteristics of the three fluorocarbons have been related to the constitution of their surfaces through study of liquid contact angles.

## APPARATUS

The device used in this investigation for rubbing one specimen against another (Fig. 2) consisted basically of a rotating turntable on which a flat specimen (platen) was mounted in the center and a balanced torque arm to which a hemispherical specimen (slider) was attached. The frictional pull on the slider was measured by a strain-gage system and recorded on a Varian G-14 recorder. The system was calibrated before each experiment by a dead-weight method. The load on the rubbing specimens was imposed by placing a 100-g weight on the torque arm directly above the slider. Measurements of kinetic coefficient of friction  $\mu_k$  were reproducible to  $\pm 0.01$ .

The circular friction path, traced by the stationary slider resting on the platen, was 2.0 cm in diameter and was generated at the circumferential rate of 1 cm/s. The starting point for each traverse, with the platen at rest, was determined with the aid of a neon indicator lamp controlled by a cam on the turntable. The traverse was automatically terminated by an abrupt separation of the rubbing specimens, while the turntable was in motion, by



Fig. 2 — Friction machine used for rubbing polymers

means of a 33-kgf-capacity alternating-current solenoid activated by the same cam. An electrical interlocking system held the specimens in a widely separated position until they were removed. The nominal length of each circular traverse was 6.3 cm, but because of the rapid response of the solenoid system the traverse was terminated just before the starting point was reached.

The disk-shaped platen specimens, approximately 1.3 cm thick by 3.0 cm in diameter, were clamped from opposite sides and near the bottom onto a rectangular brass holder or fixture. A brass screw eye attached to one end was used in suspending the assembly in the Faraday ice pail (Fig. 3). The holder was retained on the friction machine by a rectangular socket in the center of the turntable. The slider specimens were made from 1.3-cm-thick disks (2.8-cm diameter) by machining a hemispherical button of 0.6-cm radius in the center of one side of the disk. This left an integral base approximately 0.6 cm thick. The slider was mounted on a 0.6-cm-thick, 2.8-cm-diameter Teflon disk by means of machine screws. The Teflon disk was in turn mounted by means of machine screws to a small brass block provided with a stud and hand-nut for attaching the slider assembly to the torque arm of the friction machine. A small hole was drilled in the stud for use in suspending the assembly in the Faraday ice pail. A light metal cup was interposed between the Teflon disk and mounting block to facilitate handling the assembly without danger of touching the specimen or Teflon disk.

A Bausch and Lomb StereoZoom 7 microscope, having a maximum magnification of 70X, was used to examine the specimens.



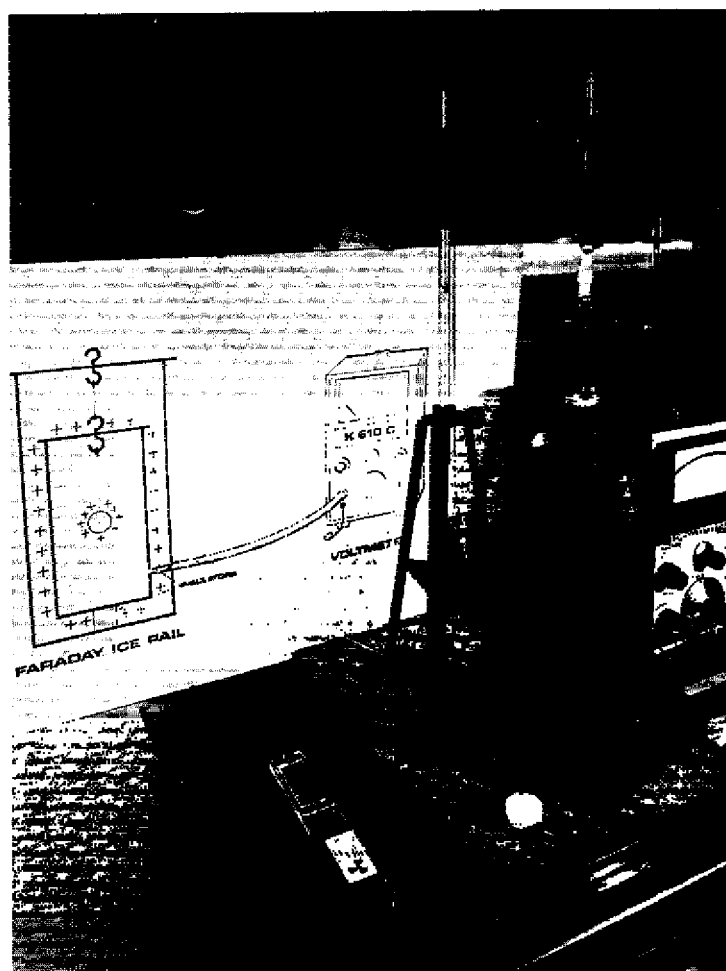


Fig. 3 — Faraday ice pail and polymer specimens

The net electrical potential on the specimens was measured by using the classical Faraday ice pail method reviewed recently by Hendricks [10a]. The Faraday apparatus (Fig. 3), made of 3.2-cm-thick brass, consisted of a grounded outer cylinder (the shield) with approximately a 14-cm outer diameter and a 30.5-cm height and an electrically isolated inner cylinder (the ice pail) with a 10.2-cm outer diameter and a 17.8-cm height, mounted concentrically within the outer cylinder on a 5-cm-thick Teflon insulator. Both cylinders had brass bottoms and brass removable covers. A steel-wire hook was attached to the underside of the inner (ice pail) cover for suspending the specimen holders. This cover was in turn suspended from the outer (shield) cover by a glazed porcelain insulator. The entire cover assembly was suspended from a grounded counterbalanced pulley system which permitted both covers to be lowered simultaneously into place. The ice pail was connected electrically to the input of a Keithly Model 610C electrometer by a rigid, low-loss coaxial connector approximately 15 cm long. The electrometer was used as a

voltmeter. The center zero was shifted to compensate for the slight potential which always resulted when the covers were lowered into place. Provision was made for grounding the ice pail through a pushbutton low-loss contactor attached to the outer cylinder.

The capacitance of the ice pail, with the coaxial connector attached, measured with a General Radio 716C capacitance bridge at frequencies of 60,  $10^3$ ,  $10^4$ , and  $10^5$  Hz, averaged 58.4 picofarads and varied less than 0.1 pF over this frequency range. The input capacitance of the Keithly electrometer, measured in the same way, varied from 25.7 pF at 60 Hz to 23.1 pF at  $10^5$  Hz. The measured capacitance at 60 Hz remained constant over the entire voltage range of the electrometer and varied less than 0.1 pF at the higher frequencies over the voltage range used in this investigation. The capacitance of the entire charge-measuring system was thus of the order of 84 pF at 60 Hz. This value approaches, but does not necessarily equal, the static or dc capacitance of the system.

## MATERIALS

A single polystyrene slider, machined from commercial-grade round stock, was used throughout this investigation. One platen was machined from commercial-grade round-stock DuPont Teflon TFE (polytetrafluoroethylene). A second platen of DuPont Teflon PFA [tetrafluoroethylene-perfluoro (alkyl vinyl ether) copolymer] was made by molding PFA powder (type TE 9704) at 800 psi and  $320^\circ\text{C}$  [11]. The third and fourth platens were machined from the same piece of commercial-grade round-stock DuPont Teflon FEP (tetrafluoroethylene-hexafluoropropylene copolymer) and designated as FEP platens 2 and 3. Selected electrical and physical properties of the specimens are listed in Table 1.

The abrasive paper used in preparing the specimens was Norton "Tufbak Adalox" Waterproof Paper Type 1, 600-A aluminum oxide made by the Norton Company, Troy, N.Y. Soft cotton diaper cloth was used for burnishing the specimens.

The two liquids used for contact-angle measurements were n-hexadecane and methylene iodide; they were chosen for reasons given by Shafrin and Zisman [9c].

## PROCEDURES

### Specimen Preparation

The specimens were placed in their respective holders for preparation in order to facilitate handling. The Adalox waterproof paper abrasive was thoroughly rinsed in a stream of singly distilled water. For abrading the platens the paper was placed on a thick, flat glass plate; polyethylene gloves were used in handling the specimen holder as the platen was gently abraded in a stream of distilled water. Successively 25 clockwise and 25 counterclockwise circular traverses were made; then the platen was rinsed thoroughly in distilled water.

Table 1  
Selected Electrical and Physical Properties of Polymers

Polymer	Volume Resistivity (ohm-cm)	Dielectric Constant at 60 Hz	Vickers Hardness*	Yield Pressure* (kg/mm <sup>2</sup> )
Polystyrene	$> 10^{16}(\dagger)$	2.5-2.65( $\dagger$ )	21.7	23.4
Teflon TFE	$> 10^{18}$ at 23°C; 50% RH( $\ddagger$ )	2.1 at 23°C( $\ddagger$ )	3.3	3.6
Teflon PFA	$> 10^{18}(\S)$	2.1( $\S$ )	3.8	4.1
Teflon FEP	$> 10^{18}(\ddagger)$	2.1 at 100 Hz( $\ddagger$ )	3.5	3.8

\*Data taken on specimens with a Tukon Modified FB Hardness Tester, using a 0.5-kg load.

$\dagger$ R. C. Weast, editor *Handbook of Chemistry and Physics*, 51st edition, The Chemical Rubber Co., Cleveland, Ohio, 1970.

$\ddagger$ D. I. McCane, p. 263 in *Encyclopedia of Polymer Science and Technology*, 13, N. M. Bikales and J. Conrad, editors, Wiley, New York, 1970.

$\S$ "Du Pont Industry News," Du Pont Co., Public Affairs Department, Wilmington, Del., Mar. 1, 1973.

The slider was abraded in the same way except that a 2.2-cm-thick sponge-rubber pad was substituted for the glass plate to help preserve the curvature of the hemispherical surface. The specimens were then burnished by substituting diaper cloth for the abrasive paper and using the same general techniques followed in the abrading process. However the specimens were rubbed against the wet diaper cloth much more vigorously and for twice the number of traverses that were used when abrading them. Finally each specimen was wiped gently with Whatman No. 40 or No. 41 ashless filter paper in a stream of distilled water. After excess water was shaken from the specimens and holders, they were dried for a minimum of 3 hours in a clean room under a well-ventilated protective cover in a laboratory chemical hood maintained at approximately 20°C and 25% to 38% relative humidity.

The burnishing reduced the roughness of the specimen surfaces and helped to remove any abrasive which might have become embedded in the relatively soft plastics. The filter paper was used to remove any lint which might have remained after the burnishing process. Examination of the prepared specimens under the microscope failed to reveal the presence of any abrasive particles or lint. In general the burnishing reduced the magnitude of the charges generated as compared with that obtained with specimens which had been abraded only, but the reproducibility of the data was somewhat improved.

#### Contact-Angle Technique

The n-hexadecane and methylene iodide used for contact-angle measurements were purified by passing them through packed chromatographic columns containing Florisil and alumina adsorbents as described by Fox and Zisman [12]. The advancing contact

angle ( $\theta$ ) of each of these liquids on the abraded and burnished platen surfaces was measured at approximately 25°C by using the drop buildup method [13] and a telescope-goniometer of the type used in earlier work [14]. Measurements were generally reproducible to  $\pm 1^\circ$ , but because of the fine scratches on the polymer surfaces that resulted from the abrading, the drops were not always round, and in these cases the reproducibility was  $\pm 2^\circ$ . This necessitated averaging measurements of several drops of each liquid and measuring each drop at least twice. Precautions were taken to ensure that the platens were free of electrical charge before measuring contact angles.

### Electrical Measurements

Measurement of the net electric potential on the specimens with the Faraday apparatus involved the following steps: each holder (with specimen attached) was suspended on the wire hook beneath the ice pail cover; the covers were lowered and the ice pail momentarily grounded to remove any charge on the holder generated during handling; the covers were raised, a brass plate was placed on the outer cylinder, and the ice pail was again momentarily grounded; the plate was removed and the specimen and covers were lowered; and the potential, of like sign and magnitude, induced on the ice pail outer surface was read on the electrometer. The total net charge  $Q$ , in coulombs, can be obtained from the well-known relationship  $Q = CV$  for capacitors, where  $C$  is the capacitance in farads and  $V$  is in volts. Since the capacitance of the Faraday apparatus and associated measuring system was of the order of 84 pF, the approximate charge in coulombs on the specimens is obtained from the product of the electrical potential in volts on the ice pail and the common multiplier 84 pF. However, for the purpose of this investigation and in the interest of simplification of the significant data, the results of the electrical measurements are reported in volts potential.

Before the specimens were installed on the friction machine, any significant surface charge was removed by bringing them momentarily near either a 10-microgram radium-226 or a 500-millicurie polonium-210 radiation source. In some instances small residual charges remained despite repeated exposure to the radiation sources. These were likely the volume charges referred to by Harper [8a], which he believed to be of little or no significance when frictional or contact phenomena were concerned. The potentials did not exceed 0.01 volt and were usually much less. They were taken into account only when very low potentials were being measured.

Each pair of specimens was rubbed together on the friction machine for ten traverses. After each traverse the electric potential of each specimen was measured in the Faraday apparatus. Two or three readings were taken on each specimen; the readings usually agreed within  $\pm 0.01$  volt or better on the most frequently used 3-volt or 10-volt ranges of the electrometer. The slider was usually measured first, since it should be more vulnerable to discharge to the atmosphere, because of its curved surface, than the platen [15]. The elapsed time between separation of the specimens and completion of the measurements was less than 30 seconds for the slider and slightly over 1 minute for the platen. Monitoring the rate of electrical discharge of the polystyrene slider in air for several minutes indicated that the loss in potential depended on the magnitude of the potential of the specimen. If it was about 2 volts, a decrease of approximately 0.04 volt

occurred during the first minute after the initial measurement. If the potential was about 0.20 volt, a decrease of only 0.01 volt occurred during the same time interval. The rate of discharge of the platens was somewhat lower. Thus differences in the magnitude of the potentials of the slider and platen which could exist at the time of measurement, because of the order in which they were measured, probably would not exceed 0.02 to 0.03 volt.

If a charged specimen was confined within the closed Faraday apparatus, the rate of discharge was only a small fraction of that in the open air. This phenomenon has been studied by others [16]. The observance of this effect in the present investigation indicated that electrical surface leakage to the specimen holders was slight.

All experimental work was performed in an electrically shielded room where the temperature was maintained between 19°C and 20°C and the relative humidity ranged between 25% and 38%.

## EXPERIMENTAL DETERMINATIONS

The frictional and electrical behavior of the polystyrene slider and TFE platen when rubbed under a force of 100 grams at the rate of 1 cm/s on the friction apparatus is shown in Fig. 4. The graphs represent the average of three experiments. The kinetic coefficient of friction  $\mu_k$  decreased from an initial value of 0.15 to 0.10 after ten traverses; most of the reduction occurred during the first four traverses. Similarly, the highest potentials acquired by the specimens occurred during the first traverse. By the third traverse the potentials had declined to a nearly constant value. As pointed out by Harper [8b], this behavior is to be expected if the rubbing materials are discharged electrically before each successive rubbing. The average deviation from the mean of the friction data was about 5%; the average deviation from the mean of the electrical data was approximately 11% and 14% for the slider and platen respectively for corresponding traverse numbers. The deviation was no greater during the earlier traverses than those occurring later. Based on the average potential acquired per traverse, the average deviation for the three experiments was 9% for both slider and platen.

The effect of replacing TFE with PFA on friction and electrical measurements is shown in Fig. 5. The graphs represent the average of three experiments. The coefficient of friction averaged 0.02 higher than that obtained with TFE; the reproducibility was about the same. On the other hand the magnitude of the potentials acquired by both slider and platen averaged over 3 times that observed when the TFE was used. Variability in the measurements was much greater at these high potentials, but the reproducibility was about the same as experienced with TFE.

Graphs representing the average of three experiments (Fig. 6) show the effect of substituting FEP for PFA. The coefficient of friction averaged 0.04 higher than was obtained with PFA. Reproducibility was about 12% compared with 5% when the other fluorocarbons were used. The magnitude of the potentials acquired by both slider and platen was only about 70% of that observed with PFA. Reproducibility of the electrical measurements was similar to that experienced with TFE. From these experiments it is

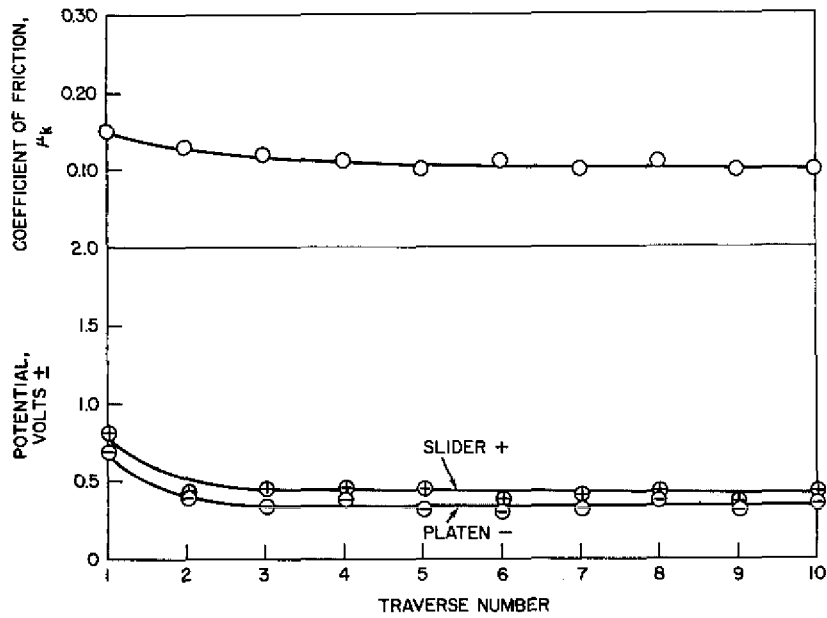


Fig. 4 — Frictional electrification of Teflon TFE and polystyrene

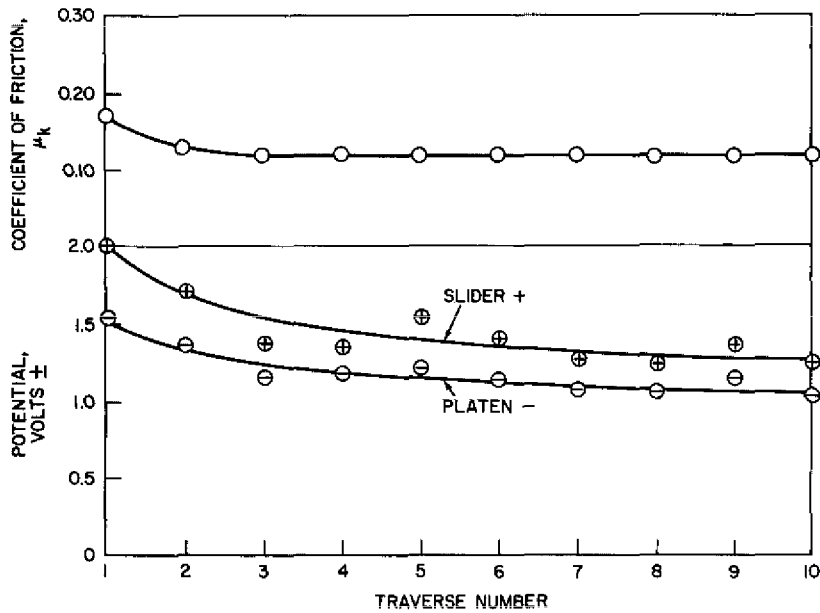


Fig. 5 — Frictional electrification of Teflon PFA and polystyrene

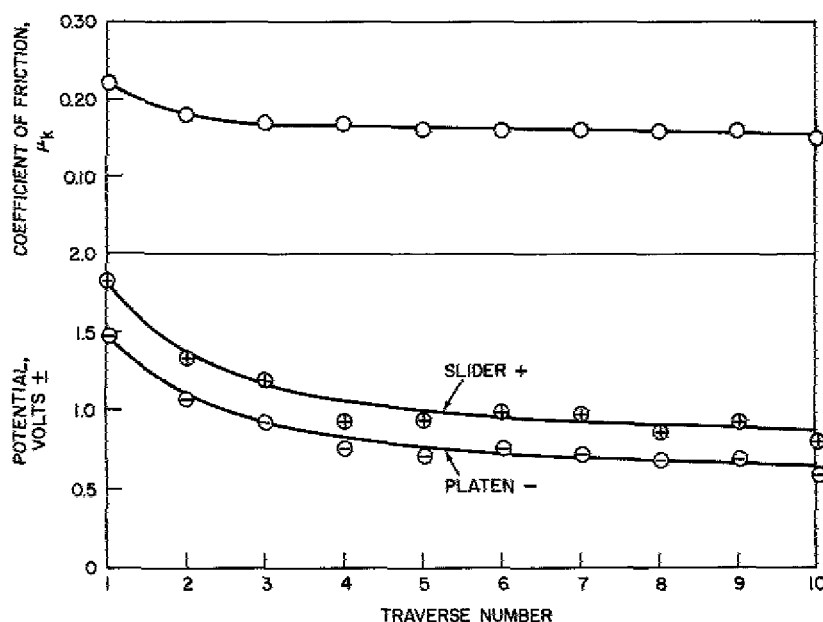


Fig. 6 — Frictional electrification of Teflon FEP and polystyrene

seen that using either copolymer resulted in an increase in both  $\mu_k$  and electrical potential. An increase in  $\mu_k$  upon substituting FEP for TFE was also observed by Bowers and Zisman [11] when they rubbed these materials against a steel slider under a much higher load. However, in contrast to the friction data just shown for PFA, they obtained a coefficient of friction with this material nearly as high as with FEP.

Examination of the platens with the binocular microscope indicated that deformation of the surface by the slider was superficial and failed to reveal any evidence of plowing or any debris. The wear tracks could hardly be discerned by direct illumination; it was necessary to examine them with the aid of reflected light. It was generally impossible to relate the appearance of the wear tracks to the magnitude of the voltage generated except when a foreign particle, wedged between the slider and platen, scratched the wear track. In this event a sudden rise in potential and in coefficient of friction almost always occurred. Usually it was impossible to detect evidence of a wear scar on the much harder polystyrene slider.

Figures 4 through 6 show that with all three types of platen specimens the potential generated on the slider was greater than that acquired by the platen. Reversing the order of measurement of the specimens did not alter the results significantly. As a check on the possible localized heating effect on the potential acquired by the slider during rubbing, a polystyrene platen was rubbed against the polystyrene slider on the friction machine. Both specimens acquired an average potential of less than 0.01 volt (after correction for residual charge); both specimens were negative. The coefficient of friction remained essentially unchanged for the ten traverses and averaged 0.52. Results of the frictional

electrification experiments seem to support Harper's [8a] belief that with insulators frictional electrification is a surface or near-surface phenomenon.

The contact-angle technique was used to determine if this method would show measurable differences in the platen surfaces which could be related to frictional electrification properties. Measurements of n-hexadecane and methylene iodide contact angles on the Teflon platens after abrading, burnishing, and drying them showed differences in the magnitude of the angles, though sometimes small, among the three types of platen materials. The relationship between the magnitude of the contact angles and that of the electrical and frictional measurements is shown in Table 2. The small difference in the n-hexadecane contact angles obtained on TFE and PFA is not significant; differences between the other values obtained are beyond experimental error. The lowest contact angles were obtained on TFE, which also exhibited the lowest platen potential and the lowest coefficient of friction. With the copolymers,  $\mu_k$  increased in the same order as the contact angles, but the magnitude of the potentials generated were in reverse order.

Table 2  
Relation of Contact Angles to Frictional Electrification and Coefficient of Friction

Polymer	Contact Angle $\theta$ (deg)		Average* Platen Potential (volts)	Average* Coefficient of Friction $\mu_k$
	n-Hexadecane	Methylene iodide		
Teflon TFE	42	93	-0.38	0.11
Teflon PFA	43	99	-1.19	0.13
Teflon FEP	46	102	-0.83	0.17

\*Average per traverse for three experiments (30 traverses).

The n-hexadecane contact angles were somewhat lower and the methylene iodide contact angles were somewhat higher than those reported by Fox and Zisman [12], Burnett and Zisman [17], and Reardon and Zisman [18] for quite smooth TFE, FEP, or PFA surfaces. The apparent discrepancy is believed to be due to the comparative roughness of the abraded specimens used in the frictional electrification experiments. The effect of surface roughness on the contact angle has been studied by Wenzel [19] and discussed by Zisman [9a]. It has been shown that on rough surfaces contact angles less than  $90^\circ$  tend to be lower and those above  $90^\circ$  tend to be higher than those measured on smooth surfaces.

#### Effects of Annealing Teflon TFE

The rather poor reproducibility of the electrical data led to consideration of possible surface-related causes. It has been pointed out [20a] that machining Teflon resins may introduce stresses in these materials which can be relieved by annealing. Similarly the abrading and burnishing may also introduce surface stresses. Although Montgomery [3]



believed that the effect of strain on quantitative frictional electrification measurements was negligible, both McCane [21] and Gillespie et al. [20b] have pointed out that TFE undergoes a change in crystallinity upon annealing. The effect of heat treating the platens on their frictional electrification by polystyrene was investigated by repeating the earlier experiments after the platens had been annealed by a process based on suggestions by Gillespie et al. [20b].

The TFE platen was abraded, burnished, and dried in air as in the previous experiments and, while still on the brass holder, was placed in a cold forced-air-circulating oven in which was maintained a slight positive pressure of air dried by passage through columns of activated alumina and Linde 4A molecular sieves. The temperature was raised to 293°C. The oven was turned off after 24 hours and allowed to cool to room temperature before the platen was removed. The cooling rate averaged 0.8°C/min down to 150°C and 0.2°C/min from 150°C to room temperature. After the platen was allowed to equilibrate for 3 hours in a chemical hood, contact angles were measured. The n-hexadecane contact angle increased from 42° to 43°; the methylene iodide contact angle increased from 93° to 98°. The liquid drops were removed by carefully absorbing them with filter paper. The platen was allowed to dry in air for several hours before frictional electrification measurements were made.

The effect of annealing TFE on friction and frictional electrification properties is shown in Fig. 7. The heat treatment lowered both  $\mu_k$  and the potential acquired by the platen. After the first traverse the potential did not decline but remained almost unchanged at an average of -0.19 volt for the ten traverses.

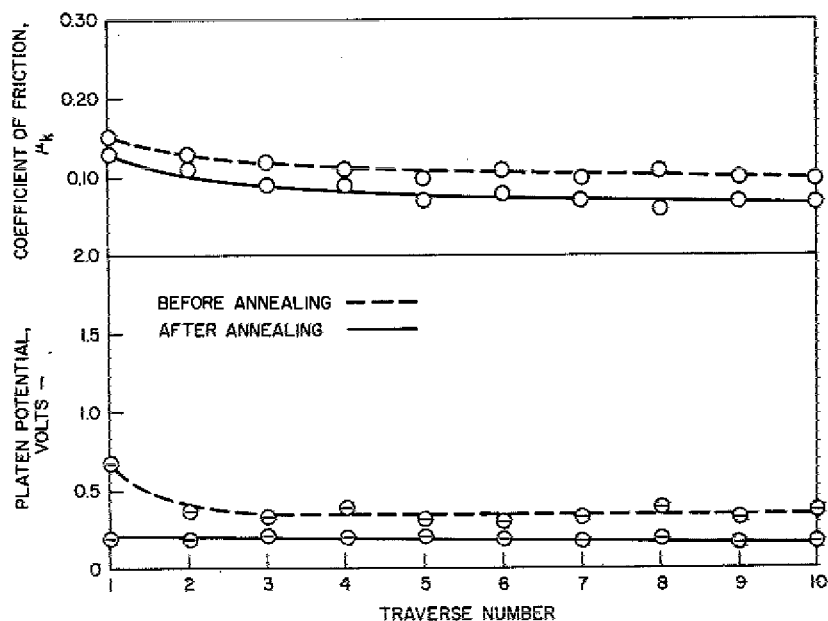


Fig. 7 — Effect of annealing Teflon TFE for 24 hours on friction and frictional electrification properties

To determine whether the lowering of the coefficient of friction and the platen potential following heat treatment was the result of changes in bulk properties or in surface properties, the annealed specimen was abraded, burnished, and dried in the usual manner and frictional electrification measurements obtained. The potentials rose slightly above the level obtained before heat treatment, but  $\mu_k$  was unchanged (Table 3). No further significant changes were observed after two additional abrading and burnishing treatments. Contact angles measured on the TFE platen after a sixth abrading and burnishing were about the same as observed before annealing.

Table 3  
Effect of Annealing Teflon TFE on Contact Angles, Frictional Electrification,  
and Coefficient of Friction

Platen Treatment	Contact Angle $\theta$ (deg)		Platen Potential (volts)	Coefficient of Friction $\mu_k$
	n-Hexadecane	Methylene iodide		
Abraded and burnished; before annealing	42	93	-0.38*	0.11*
Annealed 24 hr	43	98	-0.19	0.08
Abraded and burnished	42†	95†	-0.44*	0.08*
Annealed second 24 hr	47	106	-0.21	0.09
Abraded and burnished	45†	94†	-0.54*	0.10*
Annealed third 24 hr	48	103	-0.17‡	0.07‡

\* Average of three experiments.

† After the sixth abrading and burnishing following the last frictional electrification experiment.

‡ Based on seven traverses.

The platen was removed from the brass holder and placed in an acid-clean glass container for two additional annealing experiments.

Results of all three anneals were quite similar. Heating the fluorocarbon caused a measurable increase in contact angles (of methylene iodide in particular), a large reduction in platen potential, and a lowering of coefficient of friction. Abrading and burnishing the annealed platen restored contact-angle and platen-potential measurements to about the levels obtained on the platen before it was annealed, but the change in  $\mu_k$  appeared to be permanent.

Since light abrading and burnishing of the TFE removed much of the effect produced by heat treatment, certain changes which occur upon heating were obviously restricted to the surface of the polymer. To determine if increasing the load on the slider would cause penetration of this "layer," it was increased from 100 g to 200 g after the seventh traverse. The average platen potential per traverse was unchanged;  $\mu_k$  increased from 0.07 for the first seven traverses to 0.09 for the following eight traverses.

## Effects of Annealing Teflon PFA

The effect of annealing on contact angles, friction, and frictional electrification properties of PFA was investigated by the methods used for TFE. The PFA platen was removed from the holder, placed in a covered acid-cleaned glass container, and annealed at 283°C in the oven used previously. The annealing temperature chosen was based on long-term-aging experiences of the Du Pont Company [22].

The effect of annealing PFA for 24 hours on the friction and frictional electrification properties is shown in Fig. 8. In contrast with the behavior of the annealed TFE, heating the PFA increased both  $\mu_k$  and platen potential. In this case the potential declined with succeeding traverses. Abrading and burnishing the annealed platen before four successive frictional electrification experiments resulted in an increase in potential to a value exceeding by approximately 1 volt that acquired by the platen before it was annealed, but the process had little effect on the coefficient of friction (Table 4).

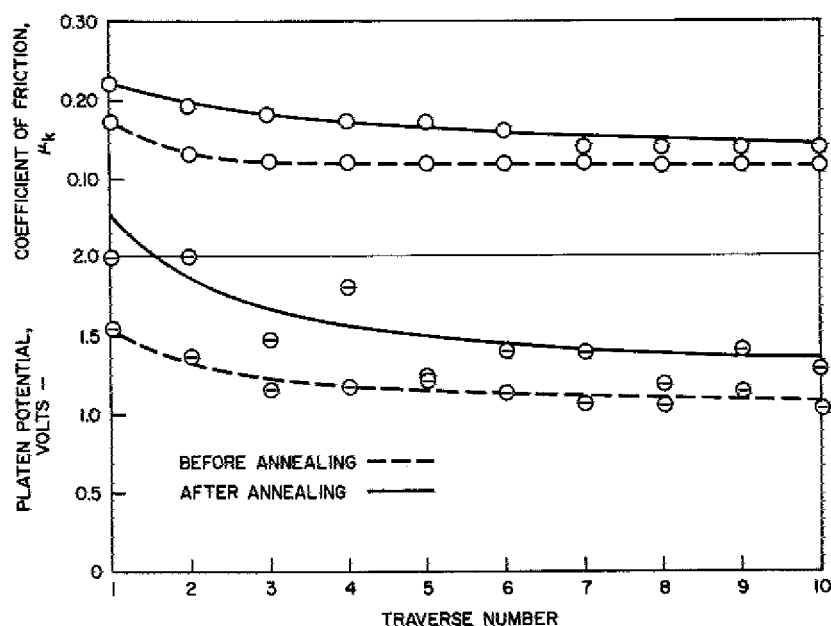


Fig. 8 — Effect of annealing Teflon PFA for 24 hours on friction and frictional electrification properties

After the previous experiments were completed, the PFA was again abraded, burnished, and dried in a chemical hood and contact angles measured. Values of 45° and 93° were obtained for n-hexadecane and methylene iodide respectively, compared with 43° and 99° obtained before the platen was annealed. It was annealed for a second 24-hour period, and contact angles were measured. The increase in  $\theta$  was much greater than that observed with TFE. Reardon and Zisman [18] also found that annealing the same type of PFA increased the n-hexadecane contact angle. The increase they observed (6°) was less than we observed on PFA (23°), possibly because their annealing temperature was 26°C lower and because they used smooth thin sheets whereas the platen surface was relatively rough.

Table 4  
Effect of Annealing Teflon PFA on Contact Angles, Frictional Electrification,  
and Coefficient of Friction

Platen Treatment	Contact Angle $\theta$ (deg)		Platen Potential (volts)	Coefficient of Friction $\mu_k$
	n-Hexadecane	Methylene iodide		
Abraded and burnished; before annealing	43	99	-1.19*	0.13*
Annealed 24 hr	---	---	-1.51	0.16
Abraded and burnished	45 <sup>†</sup>	93 <sup>†</sup>	-2.35 <sup>‡</sup>	0.16 <sup>‡</sup>
Annealed second 24 hr	66	116	-1.38	0.15
Abraded and burnished	42 <sup>†</sup>	97 <sup>†</sup>	-2.20 <sup>§</sup>	0.18 <sup>§</sup>

\*Average of three experiments.

<sup>†</sup>After final abrading and burnishing following last frictional electrification experiment.

<sup>‡</sup>Average of four experiments.

<sup>§</sup>Average of two experiments.

Both annealing experiments showed that heating PFA resulted in an increase in contact angles, platen potential, and  $\mu_k$ . The abrading process lowered the contact angles to the preannealed levels, had little effect on frictional properties, but caused a phenomenal rise in platen potential.

An unusual effect arising from the annealing of PFA was that after separation of platen and slider at the conclusion of each traverse, the platen was always at a higher numerical negative potential than the positive potential of the slider. This effect is opposite to that observed before the platen was annealed (Fig. 5). The average difference of 9% persisted after as many as four abrading and burnishing treatments of the annealed platen. This behavior is interesting in light of the fact that when the platen was fabricated [11] it had been subjected to a temperature of 320°C. The material however had been confined in a mold under pressure; contact of the copolymer surfaces with the atmosphere was limited.

#### Effects of Annealing Teflon FEP

The same general procedures used in studying the effects of annealing the TFE and PFA were applied to FEP platen 2. Because of the lower service temperature of the copolymer compared with that of TFE or PFA, the annealing temperature was reduced to 230°C, as suggested by Gillespie et al. [20a]. The platen, held in the brass holder, was heated in a Fisher natural-draft oven. The cooling rate of this oven averaged 1.9°C/min from 230°C to 100°C and 0.6°C/min from 100°C to 50°C. The platen was annealed four times: one 1-hour anneal, two 2-hour anneals, and one 24-hour anneal. The first

anneal apparently caused some dimensional changes in the platen, because it was loose in the holder after it had cooled. This was not observed after the subsequent heat treatments.

The effect of annealing FEP for 1 hour on  $\mu_k$  and frictional electrification properties is shown in Fig. 9. The heat treatment increased  $\mu_k$  (as occurred with PFA) but lowered the platen potential, as observed with TFE except that the potential declined with succeeding traverses. One abrading and burnishing of the annealed FEP was not sufficient to cause a significant increase in potential when it was rubbed against the polystyrene slider, but this single treatment caused  $\mu_k$  to return to the level obtained before the platen was annealed (Table 5). A second abrading and burnishing resulted in a substantial increase in platen potential, but there was no further change in  $\mu_k$ .

Results of the four annealing experiments and the effect of the abrading on friction and frictional electrification of FEP show that after each anneal the increase in  $\mu_k$  and the decrease in platen potential were about the same after 1 or 2 hours exposure as after 24 hours. The abrading process only partially restored the platen potential, but the frictional properties returned to the preannealed level.

Since FEP platen 2 had been annealed repeatedly and had shown some evidence of rather permanent changes, a new platen (platen 3) was machined from the original FEP stock. The effects of heat treatment of both FEP platens, involving slow and rapid cooling, on contact angles, friction, and frictional electrification properties were investigated. The results of this work are summarized in Table 6.

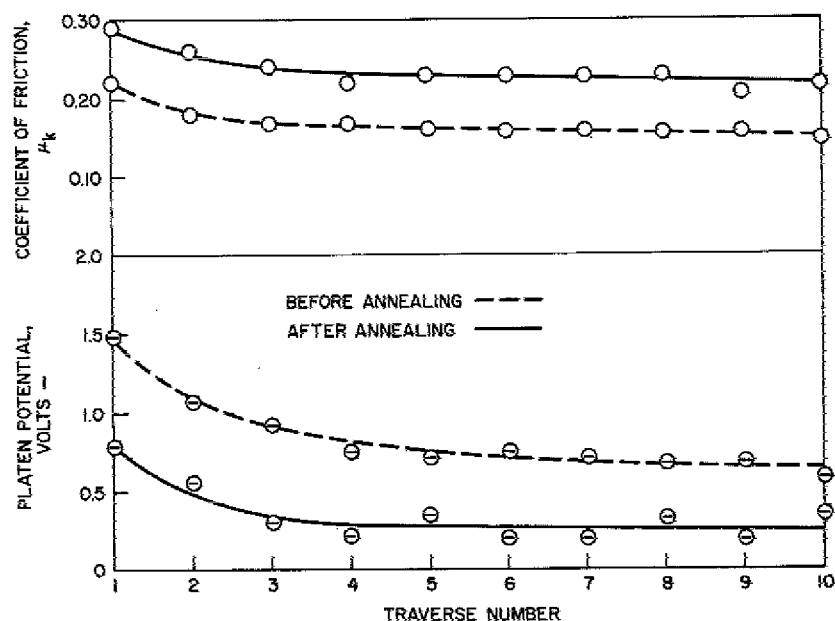


Fig. 9 — Effect of annealing Teflon FEP platen 2 for 1 hour on friction and frictional electrification properties

Table 5  
Effect of Annealing Teflon FEP Platen 2 on Frictional Electrification  
and Coefficient of Friction

Platen Treatment	Platen Potential (volts)	Coefficient of Friction, $\mu_k$
Abraded and burnished; before annealing	-0.83*	0.17*
Annealed 1 hr	-0.35	0.24
Abraded and burnished	-0.57†	0.16†
Annealed 2 hr	-0.30	0.22
Abraded and burnished	-0.79†	0.14†
Annealed second 2 hr	-0.37	0.19
Abraded and burnished	-0.55†	0.16†
Annealed 24 hr	-0.32	0.20
Abraded and burnished	-0.50‡	0.17‡

\* Average of three experiments.

† After second abrading and burnishing.

‡ Average of four experiments.

Annealing the FEP platens caused a substantial increase in contact angles, similar to that observed when PFA was annealed. The abrading process restored the contact angles to preannealed levels. With the exception of one experiment, annealing both FEP platens caused increases in the coefficient of friction similar to those observed earlier with platen 2. However the potentials attained by both platens (particularly platen 2) were considerably higher than those observed previously (Table 5). The reason for the substantial increase in potential of platen 2 may have been a result of the repeated abrading prior to the measurement of contact angles.

In discussing the effect of crystallinity of TFE on properties, Gillespie et al. [20b] pointed out that the degree of crystallinity is controlled in part by the rate of cooling of the heated material and that low crystallinity results from rapid cooling. Thus sudden cooling of a thick section results in low crystallinity near the surface. The effect of annealing the fluorocarbon polymers on contact angles, friction, and frictional electrification properties suggests that changes in crystallinity arising from the annealing process might be involved. To change the degree of crystallinity of the surfaces of the FEP platens, they were heated for 24 hours under the same conditions used in the annealing process, removed from the hot oven, and immediately plunged into distilled ice water. The heat treatment raised the n-hexadecane contact angles to about the same level observed after annealing; the methylene iodide contact angles were both 117°, compared with 125° to 130° after annealing. The coefficient of friction was slightly higher and platen potentials were slightly lower than those measured after the most recent annealings.

Table 6  
Effect of Annealing and of Heating and Quenching Teflon FEP Platens 2 and 3  
on Contact Angles, Frictional Electrification, and Coefficient of Friction

Platen Treatment	Contact Angle $\theta$ (deg)		Platen Potential (volts)	Coefficient of Friction, $\mu_k$
	n-Hexadecane	Methylene iodide		
Platen 2				
Abraded and burnished; before annealing	46	102	-0.83*	0.17*
Abraded and burnished; after previous annealings†	47	98	---	---
Annealed second 24 hr	65	130	-0.70	0.15
Abraded and burnished once	47	96	---	---
Annealed third 24 hr	59	130	-0.68	0.20
Abraded 10 times; burnished once	46	96	---	---
Heated 24 hr and quenched	60	117	-0.49	0.24
Platen 3				
Abraded and burnished; before annealing	46	103	---	---
Annealed 24 hr	63	125	-0.49	0.20
Abraded extensively; burnished once	46	96	---	---
Heated 24 hr and quenched	60	117	-0.42	0.22
Annealed 24 hr	67	124	---	---

\* Average of three experiments.

† Platen had been annealed four times (Table 5) and abraded and burnished several times after the last annealing.

After contact-angle and frictional-electrification measurements on FEP platen 3 had been completed, it was annealed for 24 hours without prior treatment of the surface. The wear track on the platen almost disappeared, which indicated that the annealing process caused physical changes of the surface. Contact angles with n-hexadecane and methylene iodide of 67° and 124° respectively agreed well with data obtained previously on annealed FEP.

## Corrosion of Brass and Copper by Fluorocarbon Polymers During Annealing

When the three fluorocarbon polymers were annealed while resting on the brass platen holders, the metal surfaces adjacent to or in direct contact with the polymers became blackened. Since the effect was most pronounced with FEP, platen 2 was annealed while resting on thin sheet brass. FEP platen 3 was abraded and burnished on both sides and annealed on a thin sheet of electrolytic copper. The brass was not as uniformly blackened as the copper; areas of the brass most remote from the copolymer were only slightly darkened. The blackened surfaces were examined by Auger spectroscopy described elsewhere [23-25]. The analysis revealed rather firmly attached fluorine in the metal surfaces. Drops of n-hexadecane spread rapidly on both the nonheated and the blackened metal surfaces. Drops of methylene iodide on the metals were not round because of surface roughness which made measurements somewhat uncertain. Despite this difficulty the contact angles were distinctly higher on the blackened areas by some  $15^\circ$  on the brass and approximately  $30^\circ$  on the copper. These increased values indicate a change in the blackened metal surfaces, quite possibly the presence of fluorine. However there were no differences between contact angle measurements on either side of platen 3.

## DISCUSSION

Harper [8c] felt that two very different charging processes exist: frictional charging and contact charging. In support of the latter, he cited the charging of an insulating material by contact with liquid mercury. Loeb [26] also believed that frictional effect is not important and that charge transfer requires chiefly intimate contact. Peterson [27] stated that most frictional charging requires only physical contact and that the term contact electrification is more appropriate. Electrification data have been reported [28] where friction between the contacting solids has been reduced to the point where it had no effect on the data.

Krupp [29] indicated that the static electrification of solids arises from two mechanisms: from contact and from deformation and cleavage.

The introduction of relative motion to solids in contact would not appear to eliminate any of the charge-transfer mechanisms that are believed operative in purely contact electrification. In discussing the complexity of mechanical and electrical processes involved in static electrification, Montgomery [3] cited elastic and plastic deformation, flow and rupture, and relaxation and creep, as well as electronic and ionic conduction, polarization, electron trapping, and other electrical phenomena. He assumes that the charging process involves primarily the transfer of electrons because of their high mobility and relative ease of detachment. Hendricks [10b] stated that when bonds within solids are strained, ruptured, or otherwise mechanically broken, electrons are released, sometimes in great quantities and over extended times. In discussing static electrification at interfaces, Inculet [10c] lists electronegativity, broadly defined as the electron-attracting capacity of an atom, as one of the molecular interface phenomena to be considered. Since fluorine is the most electronegative of all the elements [30], it is likely that the extreme electron-attracting ability of the fluorine atom is responsible for the high negative potentials acquired by the fluorocarbon polymers.



Bunn and Howells [31] and Koo [32a] have pointed out that the helical twist of the carbon-carbon chain of the Teflon TFE molecule results in an almost perfect cylinder with an outer sheath of fluorine atoms. They attribute the low coefficient of friction of TFE to weak intermolecular attraction because of the outer sheath, coupled with the rigid configuration due to the helical twist of the molecule. Sheratt [33] has reported that despite the rigidity, in crystalline sheets of TFE the molecules fold back on themselves at regular intervals. The copolymerization of perfluoro(alkyl vinyl ether) and tetrafluoroethylene (PFA) introduces perfluorinated alkane side chains connected to the carbon-carbon backbone through flexible oxygen links [22]. The copolymerization of hexafluoropropylene and tetrafluoroethylene (FEP) introduces perfluoromethyl ( $\text{CF}_3$ ) groups at random intervals. The departure from the smooth molecular profile of the TFE molecule has been shown [11,34] to be the cause of the increased coefficient of friction with these copolymers. The "rough" molecular profiles of the copolymer molecules with their side chains and exposed  $\text{CF}_3$  groups would tend to result in increased rupturing of chemical bonds. The copolymerizations resulting in PFA and FEP each have the effect of introducing  $\text{CF}_3$  groups into the surface. This greater concentration of fluorine in the copolymer surfaces would in turn result in the attraction of more electrons by the electronegative fluorine atoms, raising the negative potential acquired by these materials. Finally the introduction of  $\text{CF}_3$  groups into the surface results in a decrease of surface energy; this is shown with FEP, where  $\text{CF}_3$  groups are substituted at random for fluorine atoms in the  $-\text{CF}_2-\text{CF}_2-$  backbone [17,35], and with PFA [18], where the terminal  $\text{CF}_3$  groups of the perfluorinated side chains are oriented into the surface. As the surface energy is lowered with progressive  $\text{CF}_3$  content, n-hexadecane and methylene iodide contact angles increase. The increase in contact angles, platen potentials, and kinetic coefficient of friction observed with the copolymers compared with similar measurements with TFE is evident in Table 2.

The progressive reduction of  $\mu_k$  with successive traverses of the polystyrene slider against the fluorocarbons before annealing (Figs. 4 through 6) is believed to result from polymer orientation and possibly transfer of material from the platen to the slider [11,34], though no transferred material was observed, even with the aid of reflected light. The abraded platens presented a "flat," relatively nonreflective surface, whereas optical reflectivity from the wear tracks was quite pronounced and increased in intensity with succeeding traverses.

The factors responsible for the reduction in  $\mu_k$  during the first few traverses of the polystyrene slider are likely responsible for the concurrent reduction of platen potential. Orientation of polymer chains, which would reduce the chance of straining and rupturing chemical bonds, and the rubbing of like materials, because of the transfer of fluorocarbon to the slider, limit the platen potential.

The changes observed in contact angles, platen potentials, and  $\mu_k$  after heating the fluorocarbons may have arisen from several causes, including changes in the chemical nature of the surfaces as a result of degradation, changes in surface structure involving crystallinity, and possibly the redistribution of molecular groups [18].

The thermal degradation of TFE has been studied extensively [32b, 36-38]. Attention has been primarily on the nature of the volatile byproducts of decomposition rather than changes in the bulk of the polymer. No data have come to the attention of the authors relative to changes in the surface properties at any particular stage in the degradation process.

The relative quantities and the chemical composition of the volatile materials appear to depend on the conditions under which pyrolysis takes place. It is generally agreed that when TFE is pyrolyzed above 450°C in a vacuum, the principal product is the monomer tetrafluoroethylene ( $C_2F_4$ ). Thermal decomposition in air generally yields more carbonyl fluoride ( $COF_2$ ) than  $C_2F_4$  [32b], but the ratio somewhat depends on the type of Teflon and the temperatures involved [39, 40].

Kupel et al. [39] reported that they were unable to detect any decomposition products when TFE and FEP were held at 350°C for 4 hours. This is considerably higher than the temperatures we used to anneal the fluorocarbon polymers and suggests that very little decomposition would be expected during the annealing process. However it had been pointed out [21] that in the melt stage FEP is corrosive to most metals, so the blackening of brass and copper by this material during heat treatment was not entirely unexpected. The presence of fluorine in the blackened metal surfaces shown by the Auger studies suggests the formation of black cupric fluoride. On the other hand, contact-angle measurements on the annealed copolymer proved that any loss of fluorine to the metals had no effect on the surface energy of the FEP.

It is obvious from the increase in contact angles on the annealed fluorocarbons that heating these materials lowered the surface energy. The earlier work by Bernett and Zisman [17,35] suggests that this could have arisen because of the introduction of or increase in the number of  $CF_3$  groups or from closer physical packing of fluorine atoms in the surfaces of the copolymers. The  $CF_3$  ion has been found [39] to be the most abundant of the fluorine-containing products of decomposition of TFE and FEP in air at high temperatures. Both the coefficient of friction and the tendency of TFE to become charged were reduced by the annealing process, possibly because of the more complete shielding of the TFE backbone by an increase of fluorine atoms in the surface. Partial reduction of the shielding by abrading could explain the rise in platen potential and surface energy, but the fact that the frictional properties were not restored indicated subsurface changes also. The reduction in FEP platen potential following annealing was probably due to the reason given for TFE. The heating may have increased the "roughness" of the molecular profile, since  $\mu_k$  increased. However abrading the annealed FEP indicated that if subsurface changes had occurred, they affected potential rather than frictional properties.

The behavior of the annealed PFA was unique in that both potential and  $\mu_k$  increased. This suggests changes in the side chains. Subsurface changes obviously occurred also, because abrading the annealed surface resulted in much higher potential than was observed before the material was annealed. Again changes affecting the frictional properties appeared to extend into the subsurface, because abrading had no effect.

Based on related work by Fox and Zisman [41], Pittman and Ludwig [42] demonstrated that reducing the crystallinity of certain fluoroalkylacrylates by quenching heated

films in ice water rendered them more wettable (lowered the contact angle). Annealing them increased the contact angle. It was suggested that the annealing process resulted in closer packing of the side chains (and thus closer packing of  $\text{CF}_3$  groups) because of increased crystallization. If the large increase in contact angles upon annealing the copolymers was due entirely to an increase in  $\text{CF}_3$  groups or to other changes in the chemical nature of the surfaces, it would not be anticipated that rapid cooling by quenching would have any appreciable effect. However quenching FEP did cause a moderate reduction in contact angles, which indicated some reduction in crystallinity. The small increase in  $\mu_k$  also indicated that crystallinity had been reduced [43,44]. Obviously however most of the reduction in surface energy brought about by heating the fluorocarbons probably arose from changes in the chemical nature of the surfaces rather than from changes in crystallinity.

## SUMMARY AND CONCLUSIONS

The contact-angle technique has been useful in elucidating the nature of the surfaces of three chemically related fluorocarbon polymers. Differences in surface energies have been explained as the influence of perfluoromethyl ( $\text{CF}_3$ ) groups in the surfaces. From Fig. 10 it is seen that the relationship between surface-energy, frictional, and frictional electrification properties of the polymers varies considerably.

A number of mechanisms has been proposed by various researchers to explain the frictional electrification of solids. The study of the three fluorocarbons suggests that the most likely of the proposed mechanisms involves straining and rupturing of chemical bonds, with the result that easily displaced electrons become vulnerable to trapping by fluorine.

The rough molecular profiles of the two fluorocarbon copolymers, compared with that of TFE, present greater opportunity for the rupturing of bonds during sliding contact. This is likely the major reason for the increase in both potential acquired and  $\mu_k$ . Changes in friction and frictional electrification properties induced by annealing appear to be a function of the presence and nature of groups or side chains attached to the fluorocarbon backbone. Annealing lowers the surface energy, thus indicating an increase of  $\text{CF}_3$  groups or closer physical packing (enhanced crystallinity) of fluorine atoms in the surface.

The restoration of surface energy to preannealed levels by abrading the polymer surfaces indicated that the effects of the heat treatment were restricted to the outermost layers. Friction and frictional electrification properties of annealed and abraded polymers varied, possibly because these properties react differently to changes which may have occurred in the bulk polymer.

Rapid cooling of heated FEP had no significant effect on frictional electrification properties beyond that produced by the annealing process. The coefficient of friction increased slightly and contact angles were a little lower, signifying that quenching reduced crystallinity by a small degree. Obviously changes in properties of FEP upon annealing were primarily chemical rather than physical.

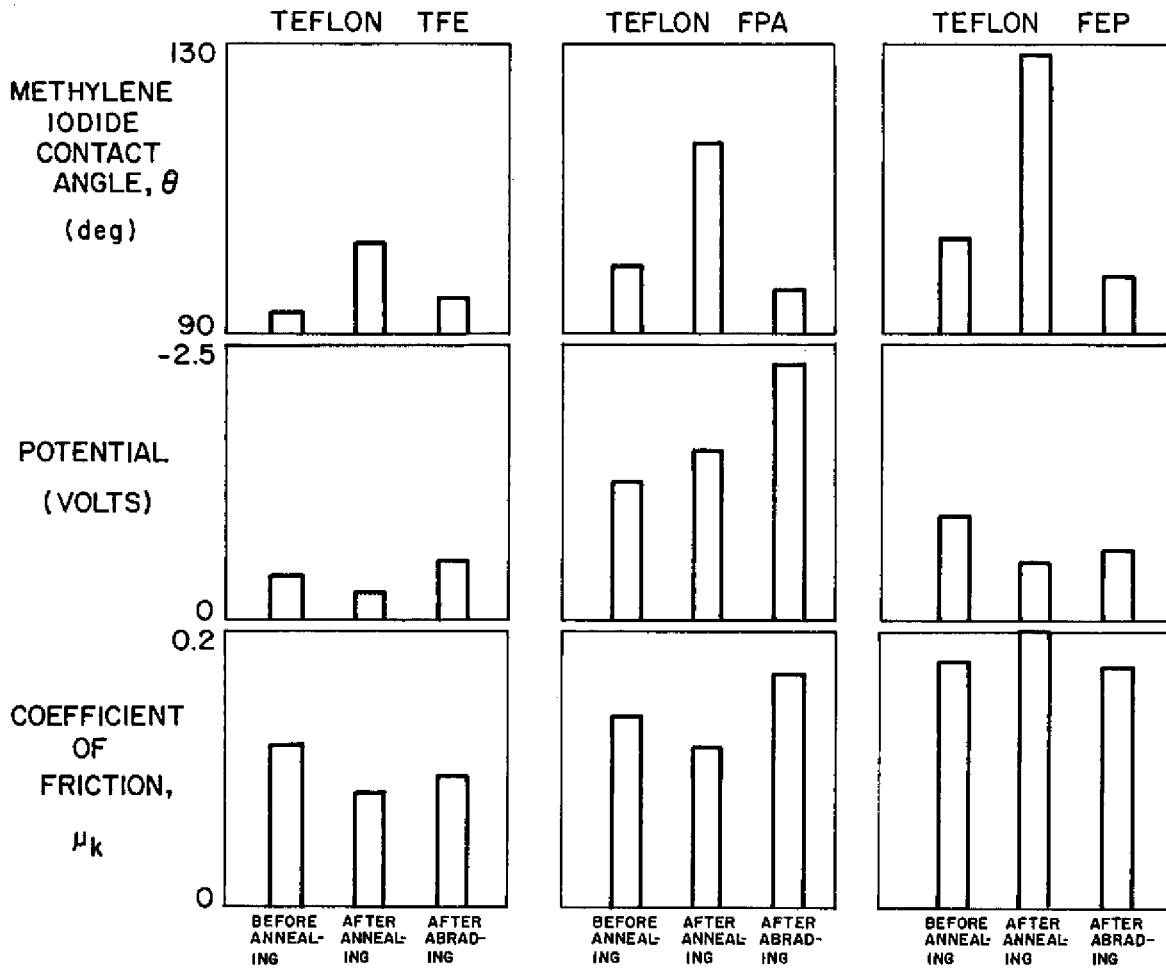


Fig. 10 — Summary of effects of annealing and abrading fluorocarbon polymers on contact angle, potential, and coefficient of friction

Brass in contact with the fluorocarbons during heat treatment was blackened. Examination of both brass and copper after contact with FEP revealed the presence of fluorine. The surface energy of the copolymer was no different in areas in contact with the copper than elsewhere.

The use of simple apparatus and similar solids does not necessarily result in significant improvement in reproducibility of frictional electrification measurements over that experienced by other workers. The study of frictional electrification of solids, like that of fatigue, obviously requires many measurements for statistical evaluation. Finally the reason precise and reproducible frictional electrification measurements with solids are difficult to obtain is believed to be that, even though extremely small forces may be involved, the act of rubbing one solid against another, in itself, alters the nature of the contacting surfaces in a poorly reproducible way.

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#### REFERENCES

1. P.E. Shaw, Proc. Roy. Soc. London, A94, 16 (1918).
2. P.E. Shaw and C.S. Jex, Proc. Roy. Soc. London, A118, 97 (1928).
3. D.J. Montgomery, Chapter 3 in *Solid State Physics*, F. Seitz and D. Turnbull, editors, Vol. 9, Academic Press, New York, 1959.
4. S.P. Hersh and D.J. Montgomery, Textile Res. J. 25, 279 (1955).
5. V.J. Webers, J. Appl. Polym. Sci. 7, 1317 (1963).
6. J. Henniker, Nature, 196, 474 (1962).
7. W.T. Morris, Plastics and Polymers, Great Britain 38, 41 (1970).
8. W.R. Harper, *Contact and Frictional Electrification*, Oxford University Press, London, 1967:
  - a. Chap. 1.
  - b. p. 55.
  - c. Chap. 4.
9. R.F. Gould, editor, *Contact Angle, Wettability, and Adhesion*, The Kendall Award Symposium honoring William A. Zisman sponsored by the Division of Colloid and Surface Chemistry at the 144th Meeting of the American Chemical Society, Los Angeles, Calif., April 2-3, 1963, Advances in Chemistry Series 43, American Chemical Society, Washington, 1964:
  - a. W.A. Zisman, p. 1 ff.
  - b. N.K. Adam, p. 52 ff.
  - c. E.G. Shafrin and W.A. Zisman, p. 145 ff.

10. A.D. Moore, editor, *Electrostatics and Its Applications*, Wiley, New York, 1973:
  - a. C.D. Hendricks, pp. 36-38.
  - b. C.D. Hendricks, p. 84.
  - c. I.I. Inculet, p. 112.
11. R.C. Bowers and W.A. Zisman, *Ind. and Eng. Chem. Product R&D* **13**, 115 (1974).
12. H.W. Fox and W.A. Zisman, *J. Colloid Sci.* **5**, 514 (1950).
13. E.G. Shafrin and W.A. Zisman, *J. Colloid Sci.* **7**, 166 (1952).
14. W.C. Bigelow, D.L. Pickett, and W.A. Zisman, *J. Colloid Sci.* **1**, 513 (1946).
15. J.L. Glathart, *Foley's College Physics*, 4th edition, Blakeston Co., Philadelphia, 1947, p. 337.
16. E.W. Anderson, L.L. Blyer, Jr., G.E. Johnson, and G.L. Link p. 424 in *Electrets- Charge Storage and Transport in Dielectrics*, M.M. Perlman, editor, Electrochemistry Soc., Princeton, N.J., 1973.
17. M.K. Bennett and W.A. Zisman, *J. Phys. Chem.* **64**, 1292 (1960); *J. Phys. Chem.* **65**, 2266 (1961).
18. J.P. Reardon and W.A. Zisman, *Macromolecules* **7**, 920 (1974).
19. R.N. Wenzel, *Ind. Eng. Chem.* **28**, 988 (1936).
20. L.H. Gillespie, D.O. Saxton, and F.M. Chapman, *Machine Design* **32** (1960):
  - a. Part 2, p. 156.
  - b. Part 1, p. 126.
21. D.I. McCane, p. 623 in "Encyclopedia of Polymer Science and Technology," **13**, N.M. Bikales and J. Conrad, editors, Wiley, New York, 1970.
22. "Du Pont Industry News," Du Pont Co., Public Affairs Department, Wilmington, Del., Mar. 1973.
23. C.C. Chang, p. 509 in *Characterization of Solid Surfaces*, P.F. Kane and G.B. Larrabee, editors, Plenum Press, New York, 1974.
24. J.C. Riviere, *Contemp. Phys.* **14**, 513 (1973).
25. E.N. Sickafus, *J. Vac. Sci. Tech.* **11** (No. 1), 299 (1974).
26. L.B. Loeb, *Static Electrification*, Springer-Verlag, Berlin, 1958, p. 166.
27. J.W. Peterson, *J. Appl. Phys.* **25**, 50 (1954).
28. G.S. Rose and S.G. Ward, *British J. Appl. Phys.* **8**, 121 (1957).
29. H. Krupp, Chap. 1 in *Static Electrification*, 1971, D.K. Davies, editor, Conf. Series **11**, The Institute of Physics, London, 1971.
30. L. Pauling, *The Nature of the Chemical Bond*, 3rd edition, Cornell University Press, Ithaca, N.Y., 1960, pp. 88-91.
31. C.W. Bunn and E.R. Howells, *Nature* **174**, 549 (1954).
32. L.A. Wall, editor, *Fluoropolymers*, Wiley-Interscience, New York, 1972:
  - a. G.P. Koo, Chap. 16.
  - b. L.A. Wall, Chap. 12.
33. S. Sherratt, p. 820 in *Kirk-Othmer Encyclopedia of Chemical Technology*, A. Standen, ed., vol. 9, 2nd ed., Interscience, New York, 1966.

34. C.M. Pooley and D. Tabor, Proc. Roy. Soc. Ser. A, **329**, 251 (1972).
35. M.K. Burnett, Macromolecules **7**, 917 (1974).
36. I.J. Goldfarb, R.J. McHenry, and E.C. Penski, J. Polym. Sci. **58**, 1283 (1962).
37. S.L. Madorsky, Chap. 5 in *Polymer Reviews*, Vol. 7, Interscience, New York, 1964.
38. J.C. Siegle, L.T. Muus, Tun-Po Lin, and H.A. Larsen, J. Polym. Sci. **2**, 391 (1964).
39. R.E. Kupel, M. Nolan, R.G. Keenan, M. Hite, and L.D. Scheel, Anal. Chem. **36**, 386 (1964).
40. K.L. Paciorek, R.H. Kratzer, and J. Kaufman, J. Polym. Sci., Polym. Chem. Ed., **11**, 1465 (1973).
41. H.W. Fox and W.A. Zisman, J. Colloid Sci. **7**, 428 (1952).
42. A.G. Pittman and B.A. Ludwig, J. Polym. Sci., A-1, **7**, 3053 (1969).
43. R.C. Bowers, W.C. Clinton, and W.A. Zisman, Lub. Eng. **9**, 204 (1953).
44. R.C. Bowers and W.A. Zisman, Mod. Plast. **4**, 139 (1963).